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IMPACT OF POTENTIAL EMISSION FROM THE BURRARD THERMAL GENERATING PLANT ON BUILDING MATERIALS IN THE GREATER VANCOUVER REGIONAL AIRSHED

A Report to

B.C. Hydro and Power Authority
5th Floor, 744 West Hastings Street
Vancouver, B.C. V6C 1A5

by

B.H. Levelton & Associates Ltd.
8805 Osler Street
Vancouver, B.C. V6P 4G1

B.H. Levelton, P.Eng.

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I. INTRODUCTION

A. Basis for the Study

B.C. Hydro and Power Authority (BCHPA) is in the process of evaluating the potential effects on the environment of operation of the Burrard Thermal Generating Plant (BTGP) near Port Moody. The composition and volume of plant emissions under various load conditions firing natural gas have been measured. A major tracer program has identified points of impingement of plant emissions and has established concentrations of pollutants (NO_x) attributable to the emissions.

The potential effects of BTGP emissions in four areas are being addressed:

1. Effects on acidity of surface water and precipitation.
2. Effects on vegetation.
3. Effects on health.
4. Effects on materials of construction.

B.H. Levelton & Associates Ltd. (BHLA) was requested to study the effects under Item 4.

B. Scope of the Study

This portion of the overall study is to cover the following:

1. A review of the chemistry of the significant pollutants (NO_x, SO_x, O_3, particulate and chloride) in the atmosphere and mechanisms by which they are removed from the atmosphere.
2. A review of the effects of the significant air pollutants in general on the deterioration of all materials of construction including metals, concrete, stone, plastics, paints and wood.
3. An assessment of the probable incremental effects of pollutants from the BTGP on materials deterioration in the Greater Vancouver Regional District (GVRD) airshed.

II. THE CHEMISTRY OF SIGNIFICANT POLLUTANTS AND THEIR REMOVAL FROM THE ATMOSPHERE

A. Basis for Discussion

The pollutants considered to be of concern in materials deterioration are nitrogen oxides, sulfur oxides, ozone, general particulate and chloride particulate. All of these materials are found naturally in the atmosphere and are not necessarily attributable only to anthropogenic sources. The BTGP contributes primarily nitrogen oxides with very small amounts of sulfur oxides to the GVRD airshed.

The chemical reactions of these compounds in the atmosphere and the means by which they are removed from the atmosphere are critical in potential deterioration of materials of construction.

B. Chemistry of the Significant Pollutants

1. Nitrogen Oxides (NO_x)

Although nitrogen oxides are emitted from a variety of natural and man-made sources, the latter are usually far more important. Combustion processes of various types account for the bulk of man-made nitrogen oxides. Typically, NO_x emitted into the lower atmosphere consists primarily of nitric oxide (NO) with nitrogen dioxide (NO_2) accounting for less than 10% of emissions. However, in the atmosphere further reactions occur which are important in potential aggressive attack on building materials. Nitric oxide is converted to NO_2 by sunlight, ozone and reactive hydrocarbons, and the NO_2 in turn is converted to nitric acid (HNO_3):

$$4NO + O_2 \longrightarrow 2NO_2 + N_2O_4$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$OH + NO_2 + \text{catalyst} \longrightarrow HNO_3$$

$$O_3 + NO_2 \longrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 + \text{catalyst} \longrightarrow N_2O_5$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

$$3\ N_2O_4 + 2H_2O \longrightarrow 4HNO_3 + 2NO$$

The species of nitrogen compounds available at any one time are numerous, but the net shift toward nitric acid production is important. This compound is water soluble and aggressive toward virtually all construction materials. Thus, measurement of NO_x in the atmosphere provides an indication of the potential aggressiveness of the atmosphere (HNO_3 is not normally measured in monitoring programs). The actual damage which NO_x may cause depends on how it is removed from the atmosphere and what degree of conversion to HNO_3 has occurred.

The nitrogen oxides and the nitric acid formed from them may react with ammonia in the atmosphere to form ammonium nitrate which can be a corrodent in specific cases (usually involving copper alloys). It is not normally considered to be a serious agent in deterioration of building materials.

2. Sulfur Oxides

Like nitrogen oxides, sulfur oxides may be formed by both natural and anthropogenic processes. Man-made sulfur oxides result primarily from combustion processes which include power generation, home heating, transportation, chemical and petrochemical plants and mineral processing plants.

Sulfur dioxide (SO_2) is the principal oxide emitted by combustion processes. It is soluble in water yielding a weak acid which attacks building materials. Sulfur dioxide in the atmosphere undergoes a range of reactions which terminate in formation of sulfuric acid:

$$SO_2 + 1/2\ O_2 \longrightarrow SO_3 \text{ (sulfur trioxide)}$$

$$SO_2 + O_3 \longrightarrow SO_3 + O_2$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \text{ (sulfuric acid)}$$

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + 1/2\ O_2 \longrightarrow H_2SO_4$$

The acid is water soluble and is scrubbed from the air by rainfall as being removed by dry deposition.

Sulfuric acid reacts with ammonia to form ammonium bisulfate particulate, a major component of airborne particulate in industrialized areas.

The oxidation of sulfur dioxide to the trioxide proceeds more slowly than the corresponding oxidation of nitric oxide.

3. Ozone

Ozone in the atmosphere occurs primarily from reactions between oxygen and various organic compounds. Its major effect in materials deterioration rests with its activity in oxidizing nitrogen and sulfur oxides to the corresponding acid forms. By itself, ozone will attack rubber, plastics and leather and so may be regarded as a pollutant capable of causing materials deterioration, though the overall effect is probably secondary to its oxidative reactions.

4. Particulates (other than chlorides)

Particulates in the atmosphere encompass the entire range of substances found on earth. They range from common dirt to carbon and include material originating at ground level as well as solids formed by reaction in the atmosphere (ammonium nitrate and ammonium bisulfate).

When particulates are removed from the atmosphere by dry and wet deposition they have a number of effects on construction materials:

(a) They soil materials, an aesthetic problem.

(b) They may contribute physical effects to normal corrosion reactions which accelerate attack.

(c) They may adsorb pollutants in the atmosphere and release them when deposited on a structure, thereby providing localized concentration of pollutants.

(d) They retain moisture and prolong destructive action.

5. Chloride Particulate

All air contains some chloride particulate, originating primarily from wave action on the oceans, but with a significant amount derived from salt deposits on the land. The amount of such particulate varies widely, typically being high near the shoreline and low in the interior of land masses.

In the Vancouver area there are a large number of boilers burning hog fuel derived from seawater-floated logs. At furnace temperatures the sodium chloride in the fuel is volatilized and condenses as a fume as the boiler gases cool. This chloride is a significant contributor to background chloride and for specific plume impingement it may represent the largest source of atmospheric chloride.

Field tests have shown that hog fuel boilers also emit ammonia and ammonium chloride particulate can be formed in the stack plumes.

In the airshed in question bulk loading of potash (KCl) contributes intermittently to atmospheric chloride and the chlor-alkali industries emit small amounts of chlorine, chloride, hypochlorite and chlorate which eventually end up as chlorides.

Chloride particulate can affect construction materials in two ways. First, the chloride ion is a promoter of corrosion of most metals, typically leading to pitting attack and to stress corrosion cracking in a suitable environment. Second, chloride ion combined with sulfuric or nitric acids leads, in effect, to hydrochloric acid mixed with other acids. Hydrochloric deteriorates metals and many materials of construction.

6. Carbon Dioxide

Carbon dioxide is not normally considered to be an aggressive air pollutant because it is a normal constituent of air. Even in a "clean" air, carbon dioxide will lead to deterioration of certain building materials. Carbon dioxide in water converts to carbonic acid which can dissolve marble and limestone and which will attack the feldspar component of granite.

The actual contribution of carbon dioxide to materials deterioration is not known. Certainly, other acid gases in polluted areas have accelerated materials attack well beyond that attributable to carbon dioxide, and probably the bulk of damage is caused by such pollutants. However, carbon dioxide provides a background materials attack which exists in polluted and unpolluted environments.

C. Removal of Pollutants from the Atmosphere

1. Wet Deposition

Wet deposition of both gaseous and particulate pollutants involves either absorption into or entrainment by water droplets. Where acid gases (nitric and sulfuric) are present an acid rain results. This is a commonly recognized phenomenon resulting from air pollution, but probably has only a minor effect on materials deterioration where

precipitation is significant unless pollution is extremely severe. This is exemplified by a pH of 4.9 in Vancouver precipitation and a pH of 4.3 in Southern Ontario rain (20). Such deposition of acid gases in solution usually results in a very low acid concentration, so low that direct effects on materials are minimal. In effect, while the pollutant is scrubbed out, the resulting solution is so dilute (particularly in Vancouver) that it is not markedly corrosive. The dissolved acid does contribute to residual acidity of the ground and bodies of water where the acid can concentrate. However, on structures and the like, precipitation keeps washing away dissolved acid, and the heavier and longer the rainfall, the more dilute is the solution.

The above situation suggests that objects which are well exposed to rain should corrode less than those which are dampened by rain but are not continually washed by it. This phenomenon has been reported in texts on corrosion technology. If wet and dry deposition processes account for equal amounts of nitric acid removal (20), then the wet deposition should be about 6.6 g/m^2 y (see Item 2 following).

The relative contributions of sulfur oxides and nitrogen oxides on overall acidification of rain depend on the degree of conversion of nitrogen oxides to nitric acid. Since the nitrogen oxide reactions involved require considerable time, it is probable that the effect of any emission source on increasing acidity of precipitation will be significant only after the emission has had a chance to mix well with the surrounding air mass.

Vancouver data for 1976 (20) show sulfur dioxide emissions at 47,000 tons per year and nitrogen oxide emissions at 63,000 tons per year. The resulting hydrogen ion equivalents are 1473 and 1375 tons per year for sulfur dioxide and nitrogen oxides respectively (nearly the same). If both types of oxide are equally soluble in water and are absorbed at the same rate, then any resulting acidity can be attributed equally to the two components.

2. Dry Deposition

Dry deposition of gaseous pollutants can occur in several ways:

- by direct reaction with plants and other materials;
- by absorption from air to a wet surface, such as a dew-wetted structure;

- by deposition with or onto an adsorptive solid such as carbon, oil soot, etc.

Concord Scientific (20) have concluded that there will be little deposition of nitrogen oxides by either wet or dry mechanisms in the GVRD airshed. Nitric acid produced in the atmosphere from such gases will be deposited, principally at some distance from the plant because of time required for conversion of oxides to the air.

Concord (20) have estimated the following incremental effects of the BTGP emissions within a 50 km radius of the plant:

- Dry deposition of nitric acid over background - 0.50%

- Wet deposition of nitric acid over background - 5%

These values are considered to be conservative by Concord. Actual dry deposition rates of nitric acid are estimated to be:

- Background dry deposition - 6.6 g/m^2 y

- BTGP contribution (max) - 0.030 g/m^2 y

In Europe (1) over a very large land area the dry deposition of nitrogen oxides expressed as nitrogen is about 0.50 g/m^2 y which corresponds to 2.25 g/m^2 y of nitric acid. This measured value is lower than the 6.6 value estimated by Concord. The wet and dry deposition of nitrogen compounds (primarily acid) are equal. Concord (20) have assumed the same situation.

It is likely that dry deposition mechanisms lead to the bulk of materials deterioration. These processes allow gases in the air to come to equilibrium with an absorbing solution, thereby forming a much more concentrated solution than results from rainwater scrubbing of the air. If this premise is correct, the most serious materials deterioration should occur where:

- high pollutant levels exist;

- time of surface wetness is high but rainfall is low;

- the surface is dirty and protected from direct rainfall.

Experience has shown that where combinations of these exist, serious attack on materials occurs.

Thus, in predicting the effects of air pollutants on materials deterioration, it is necessary to consider how the materials are exposed to the atmosphere, what the precipitation patterns are, and what levels of pollutants exist. The most severe attack (if any occurs) will exist in areas contaminated with dirt (particulate) which are damp for long periods of time and which are not washed thoroughly by rainfall.

III. EFFECTS OF POLLUTANTS ON MATERIALS OF CONSTRUCTION

A. General

The effects of air pollutants on deterioration of construction materials (including fabrics, etc.) are difficult to isolate for each polluting compound. For example, sulfur oxides converted to sulfuric acid and absorbed in water on metal will cause more corrosion than the water alone would, and if chloride particulate is added the attack is even further accelerated. If inert particulate also settles on the metal it almost certainly will prolong the period of corrosiveness by holding moisture, and for certain metals (aluminum typically) the solids may promote specific localized attack by controlling access of oxygen to the metal.

In the following sections, the effects of various pollutants on a range of materials are discussed. Correlations between damage and pollutant level deal with a single pollutant. Where multiple interactions are possible, reported deterioration becomes qualitative in nature rather than quantitative.

Considerable detail has been provided for sulfur oxides because the outdoor effects of these compounds have been documented best. The BTGP will not emit significant amounts of sulfur oxides so that incremental effects of such emissions will play no part in this evaluation. However, the general relationships which have been developed for sulfur oxides should hold for other acidic gases and for corrosive particulate as well, and provide some indication of how pollutants can affect materials.

It has become necessary to differentiate between outdoor and indoor corrosion mechanisms. Outside deterioration is normally associated with physical moisture deposition, either by precipitation or by adsorption at high moisture contents. Indoor attack is confined to "dry" surfaces where pollutants act directly with materials, probably aided by adsorbed moisture.

It is of interest to note that Battelle (2) has found for indoor exposures that strong synergistic effects do exist for low levels of pollutants in combination. Single gas tests in the laboratory bear no relation to reactions produced by natural environments. Battelle found for electronic components that critical ingredients of a polluted gas mixture were:

- a form of reactive sulfide (H_2S);

- a reactive chloride constituent;

- a strong oxidizing constituent such as NO_2 or O_3

Interestingly, sulfur oxides have little effect because indoor levels of this compound are generally low, presumably because of various absorption mechanisms.

It can be seen, therefore, that materials deterioration resulting from air pollution is a complex matter and that it is difficult to establish the additive effect of any specific component.

B. Sulfur Oxides

1. On Metals

Extensive field testing has shown that for ferrous metals exposed to normal urban and industrialized atmospheres (outdoors, not indoors) the major factors affecting corrosion rate are sulfur oxide concentration, time of wetness and temperature. Time of wetness depends on rainfall patterns, on relative humidity, on surface orientation and on particulate loading. The time of wetness for a roof overhang, for example, is reported to be about twice that for a vertical wall.

In general, corrosion of metals does not proceed in the absence of moisture. However, moisture need not be present as a physically obvious layer of water. There exist critical relative humidities for most metals below which corrosion does not occur. For ferrous meterials rusting in the atmosphere starts slowly at 60% RH, at 75-80% RH there is a sharp increase in corrosion rate, and at 90% a third increase in rate occurs. Aluminum does not begin to corrode until 80% RH is reached.

Sulfur oxides increase corrosion rates of metals by being absorbed on the moist metal surface in a form of dry deposition. The acid strength which results may be quite high because the water layer can come to equilibrium with the gas-phase pollutant.

An ASTM study (6) of steel corrosion rates at 57 U.S. test sites produced the following correlation:

$$\text{corrosion} = 325\sqrt{t}\, e^{(0.00275A - \frac{163.2}{B})}$$

where corrosion = thickness loss, μm

t = time, years

A = average SO_2 concentration, $\mu g/m^3$

B = relative humidity, percent

This type of correlation has been found to hold generally for a number of different tests.

Mild steel corrosion rates throughout Canada and the United States have been shown to depend primarily on sulfur oxide concentrations, or the observed corrosion rate correlates with sulfur oxides. It is possible that sulfur and nitrogen oxides are usually present in roughly the same ratio so that the effect of nitrogen oxides is screened. This theory is not supported by laboratory studies (5)(11) but the work of Battelle (2) may explain some of the discrepancies.

A steel corrosion rate of 1.6 mpy (one mil = 0.001 inches) over 10 years was measured for Halifax when the SO_2 level was 0.223 ppm (a very high value). Note that the Halifax site would have significant chloride levels, the effect of which cannot be established at present.

Stainless steels are little affected by normal sulfur oxide levels except where chloride particulate deposition occurs. In these cases, some of the stainless steels may pit. Note that stainless steels may corrode severely in the absence of sulfur oxides where wet chloride containing deposits exist.

Galvanized steel depends on formation of a basic zinc carbonate film for corrosion protection. In unpolluted rural atmospheres this film gives excellent protection. In industrialized atmospheres, acidic moisture destroys the film and the zinc layers dissolve quickly.

Guttman (8)(2) showed that the corrosion of zinc metal in the atmosphere could be predicted by:

$$y = 0.0014\ [0.005461A^{0.8152} * (B + 0.02889)]$$

y = thickness loss (cm)

A = time of wetness (hr)

B = SO_2 content during wet period (ppm)

The correlation did not hold where high chloride levels were present and provided an additive corrosive effect.

Aluminum alloys have generally good resistance to sulfur oxides. The oxide film is stable between pH 4.5 and 8.5 (11). Haynie et al (11) found that stressed 7000 series T6 alloys were mildly susceptible to stress corrosion cracking in SO_2-NO_2-O_3 environments. SO_2 was considered to be the aggressive component.

Copper and copper alloys are generally resistant to atmospheres containing sulfur oxides. An initial rapid reaction occurs until a protective patina of basic copper carbonate is formed. Average corrosion rates for metal roofs are 0.05 mpy in an industrial atmosphere and 0.03 and 0.02 mpy in marine and rural atmospheres respectively.

2. On Concrete

Concrete is attacked by sulfuric acid leading to formation of calcium sulfate. Deteriorated concrete exhibits typical white deposits of sparingly soluble calcium sulfate (gypsum) and its subsequent hydration may lead to swelling of the mass with subsequent cracking. It is probable concrete is attacked seriously only where stack plumes containing sulfur oxide impinge on it. Elsewhere, action is slight.

3. On Stone

Limestone (or marble) may be heavily corroded in polluted atmospheres. Recent studies in Greece have shown that statuary has been so badly damaged by the polluted atmosphere in the past 30 years, that many works of art have been moved inside. Buildings in England constructed from marble and sandstone have undergone serious deterioration from pollution. Unfortunately, while much of such damage has been ascribed to sulfur dioxide, no clear evidence of effects of individual pollutants has been developed.

Haynie (11) showed that white Cherokee marble was only slightly damaged by high concentrations of SO_2, NO_2 and O_3. According to laboratory test data, marble under wet urban conditions should waste at only one mm in 30 years.

This loss is well below observed damage in many areas, indicating that other factors are important. It is probable the synergistic effects of carbon dioxide and chlorides on other pollutants have not been considered.

It is worthwhile commenting here that building stones including granite are attacked in nature by lichens through a mechanism involving release of carbonic acid and a degree of physical wedging. In very polluted atmospheres lichens do not grow and so pollution may actually inhibit some natural attack.

The effects of freezing and thawing cycles on building stones has not been quantified. Undoubtedly, in colder climates such action may contribute significantly to deterioration, particularly where chemical action by pollutants has weakened the stone.

4. On Paint and Plastics

Sulfur dioxide can cause damage to undried and dried paint films. Haynie (11) found that dried oil-base paint is severely deteriorated in combined exposure to SO_2, NO_2 and O_3. In laboratory tests only SO_2 and relative humidity were found to correlate with weight loss. Since weight gains also represent deterioration, the effects of NO_2 and O_3 may be significant.

Vinyl and acrylic coatings, and vinyl siding were little affected by sulfur oxides.

C. Nitrogen Oxides

1. On Metals

The effect of nitrogen oxide pollutants on metals has not been clearly identified. To date, correlations of steel corrosion have been based on SO_2 level and time of wetness. Since nitric acid is water soluble, and since the nitrogen oxide precursors of the acid are present in the atmosphere at roughly the same levels as SO_2, it is reasonable to assume nitrogen oxides will contribute to metal corrosion. It is possible that the relatively constant ratio between SO_2 and NO_2 has masked the effect of NO_2 and that correlations of corrosion rate based on SO_2 levels in fact incorporate NO_2 levels in the constants. An alternative explanation is that nitrogen oxides are disposed of primarily by wet deposition and so contribute little to metal corrosion which probably is governed chiefly by dry deposition processes.

Soderlund (1) indicates that the overall acidification effect of NO_2/SO_2 is in the ratio of 1/3. Concord Scientific (20) for Vancouver suggest that the overall acidifications should be roughly equal. This probably results in part from the fact that the NO_x/SO_2 ratio in Vancouver is much higher than the same ratio for the Europe Test area. If the overall acidification ratio holds for dry deposition, then it might be expected that nitrogen oxides contribute 50% of the damage attributed to acid gases, i.e. the same as for sulfur dioxide.

All atmospheric corrosion data for metals indicate that nitrogen oxides have little effect on corrosion rate. This is contrary to the expected effect of acidification by dry and wet deposition. As was explained in Section III.B.1., the effect of nitrogen oxides may be included in correlations for corrosion by sulfur dioxide because the ratio of the two pollutants tends to remain relatively constant throughout the atmosphere. The correlations are not precise and the effect of nitrogen oxides can easily be masked.

A very conservative estimate would allocate 50% of the corrosion of metals to nitrogen oxides. This, however, is not correct because even in the absence of sulfur and nitrogen oxides, metals will corrode. Considering the atmospheric corrosion data of Table I, Section IV, it may be assumed that the City of Nelson represents an unpolluted atmosphere while Trail is a typical polluted area with roughly the same precipitation. The corrosion due to acid gas (SO_2) appears to be about two times that due to water and other factors in the absence of acid gas. This is a very rough estimate but it is the only available basis on which assumptions can be made. Thus, in this report it is assumed that, of observed atmospheric corrosion, 67% is due to acid gases unless acid gas levels are very high (greater than 0.10 ppm). Half of this, at the most, is due to nitrogen oxides, or, rather, to nitric acid formed from nitrogen oxides.

For mild steel, the above relation should hold reasonably well. For stainless steels and aluminum it is probable any nitric acid would aid in maintaining passivity rather than accelerating attack. Galvanized surfaces will be attacked by nitric acid much as by sulfuric acid.

The action of nitric acid (and nitrates) on corrosion of copper and copper alloys is potentially more serious than that of sulfuric acid. There have been reports of severe corrosion of pole-line hardware on high-voltage transmission lines where corona discharge can lead to formation of ozone and nitrogen oxides. Bell Telephone (13) report stress corrosion cracking of nickel-brass wire springs caused by airborne nitrates in the Los Angeles area. Electronic components inside buildings have been reported to be seriously attacked by mixtures of NO_2, O_3, moisture and chlorides. Attack occurs at levels of NO_2 in the region of 0.20 ppm. No data are currently available on the levels of O_3 and chlorides involved.

A Japanese laboratory study (14) found that NO_2 had more corrosive effect than SO_2 on wet copper.

2. On Concrete

In theory, nitric acid is more aggressive toward concrete and limestone than is sulfuric acid because the former produces soluble calcium nitrate as a reaction product while the latter produces relatively insoluble calcium sulfate. The calcium sulfate may, however, have a physical effect in spalling off deteriorated material. Actually, sound concrete does not appear to be significantly attacked by normal pollution.

3. On Stone

This was covered under Item B.3. above.

4. On Paint and Plastics

Item B.4 discussed the effects of SO_2, NO_2 and O_3. Note that NO_2 may cause weight increases in dried paint films, presumably because of reaction with film components, a form of deterioration.

D. Ozone

The direct effect of atmospheric ozone on building materials is confined primarily to organic materials. Ozone will cause deterioration of paint films, plastics and synthetic fibers by direct oxidation. In such highly polluted areas as Los Angeles, leather is reported to be deteriorated by ozone.

It should be recognized that the BTGP does not emit ozone, and it is only the reaction between atmospheric ozone and nitrogen oxides which can lead to materials deterioration. Combined with sulfur gas species, ozone can lead to accelerated attack on electric components.

E. Particulate Material

Except in rare cases, particulate material itself is not aggressive toward materials of construction. It may cause erosion in the extreme case where wind-blown dusts impinge on buildings and objects. The principal function of particulate from the atmosphere is to absorb corrodents and to hold moisture on surfaces long after they would dry if clean. In this way deposits of dirt promote corrosion through physical action.

F. Chloride Particulate

Any chloride salts and other salts such as nitrates and sulfates can accelerate corrosion and deterioration in neutral water or in acidic water films. As has been pointed out earlier, the chloride ion is aggressive in metallic corrosion, generally much more aggressive than the nitrate and sulfate ions.

The presence of chloride in the atmosphere can so affect corrosion/deterioration rates that accepted correlations may be valueless (7). Thus, monitoring of the atmosphere for acid gases may not provide a meaningful indication of potential corrosiveness if the level of chloride is not also known.

IV. PRESENT DETERIORATION OF MATERIALS IN THE GVRD

Before the potential additive effects of BTGP emissions can be assessed, it is necessary to establish existing deterioration rates and relate them to air pollutant levels. There are no accurate data for corrosive rates correlated with air pollutant levels in the GVRD.

Table 1 shows corrosion data for a number of cities in Canada. The effect of salt is demonstrated at the two Victoria sites. With roughly the same SO_2 levels (both low) the corrosion rate in the City is twice that at Pedder Bay, presumably because of the higher salt level. The data for Nelson which has little airborne chloride may contradict the relation, but other factors in the test program may have affected results.

In Vancouver Harbour, the sodium chloride atmospheric levels have ranged from 0.001 to 0.005 ppm (2 to 10 $\mu g/m^3$). These values would not be typical for the City and probably would be confined to the harbour and to the areas northwest and west if the predictions of J.H. Emslie are used (18). It is probable levels in the range of 1.0 to 2.0 $\mu g/m^3$ would be reasonable for Vancouver generally (similar to Victoria, Pedder Bay).

The corrosion/deterioration resulting from specific gaseous pollutants has never been established for Vancouver. It is well known that galvanized downpipes near petroleum refineries do not last as long as those in the western part of the City, and they in turn do not last as long as downpipes in rural areas.[1] This reduced life in specific areas probably is associated with sulfur oxide levels, and, if theory is correct, with nitrogen oxide levels. It is reasonable to expect nitrogen oxides to be formed in any combustion process which evolves sulfur oxides, although the reverse is not necessarily true.

There are no data on deterioration of building materials other than metals. Concrete structures have not been significantly damaged over many years and building stone appears to have been unaffected by atmospheric contaminants. It has been pointed out that carbon dioxide may be a more significant source of deterioration of concrete and marble than the sulfur and nitrogen oxides, and it should be recognized that concrete paste constituents are leached by soft waters (rainwater).

Bronze statuary is little affected by the atmospheric contaminants, merely acquiring the desired protective patina, which is a form of corrosion product.

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[1]Data from private files of B.C. Research Council and B.H. Levelton & Associates Ltd.

TABLE I

CORROSION OF MILD STEEL IN THE ATMOSPHERE

SITE	SO_2 LEVEL (ppm)	SALT LEVEL ($\mu g/m^3$)	CORROSION RATE (mpy)	
			2 YEARS	10 YEARS
Montreal	0.056	-	1.21	0.39
Halifax	0.18	-	2.73	1.64
Saskatoon	0.0045	-	0.55	0.18
Victoria, City Site	0.0073	4	1.10	-
Pedder Bay	0.0035	1.9	0.60	
Nelson	0.0035	-	0.60	
Trail	0.04	-	1.88	

TABLE 2

ACID GAS LEVELS IN GVRD ATMOSPHERES

PERIOD	GAS LEVELS (ppm)	
	SO_2	NO_2
Annual average	0.01	0.02 - 0.03
24-hour average[1]	0.01 - 0.17	0.05 - 0.07
1-hour average[1]	0.03 - 0.51	0.11 - 0.19

[1]Range of maximum average values from GVRD, 1980, Table 4-2, ESS-39 Report

It is difficult to ascribe specific contribution to corrosion to the various air pollutants in the GVRD. Data from BCHPA Report ESS-39 (19) on acid gas levels is given in Table 2. Higher values may occur, but these probably represent the District adequately. The ratios of concentrations is reasonably close to the ratio computed from estimated total emissions in the Lower Mainland. If nitrogen dioxide is considered to contribute 50% of all bare steel corrosion attributable to No_x and SO_x in the GVRD, and if these acid gases are responsible for 67% of atmospheric corrosion, then the corrosion attributable to NO_x is about 0.10 mils per year (0.25 mpy x 0.67 x 0.50). This assumption is very broad, because, as has been pointed out earlier, the precise effect of NO_x on atmospheric corrosion has not been established. Indeed, it has been indicated that the effect of NO_x is negligible. Therefore, the assumption of 0.10 mpy is extremely conservative.

V. POTENTIAL EFFECT OF BTGP EMISSIONS ON MATERIAL DETERIORATION

A. General Discussion

The BTGP emits only one pollutant of significance in materials deterioration, nitric oxide. The incremental effect of this emission depends on the increase in existing levels resulting from its emission either generally or at specific points of impact, the percentage conversion to nitric acid and its dissipation into the airshed.

Brotherston and Emslie (19)(Table 5-3) show probable contributions of NO_x and NO_2 from the BTGP and measured background NO_2 at GVRD air quality stations. These contributions are calculated from specific emission impingement tests during atmospheric conditions favouring impingement. These data are not suitable for estimating effects on materials deterioration because they are for short terms and corrosion is a time dependent phenomenon. Accordingly, it is considered preferable to consider the effects on materials deterioration of nitrogen oxides when they are dissipated in the total GVRD air mass. This is an appropriate procedure because the nitrogen oxides are not converted to nitric acid near the BTGP and so would have little effect on nearby points of impingement.

The total contribution of the BTGP operating at capacity to the NO_x loading in the GVRD airshed is about 3700 tonnes per year if all six units run continuously (19). This compares with a projected NO_x total emission for 1985 of some 77,000 tonnes in the Region (assume this figure includes the BTGP contribution). Thus, if the plant were to run continuously and the NO_x emission were uniformly distributed, it would affect NO_x levels by about 5%. Referring to Concord's data in Table 3 of their October 1981 Report (20), the GVRD 1973 emissions of acid gases expressed as hydrogen ion equivalents are:

- SO_2 total	- 1473 tonnes per year
- NO_x total	- 1375 tonnes per year
- NO_x from BTGP	- 80 tonnes per year
- NO_x from BTGP % incremental	- 3

The data from Concord agree reasonably well with the calculation above.

Since it has been assumed metal corrosion is caused 67% by acid gases in the lower gas concentrations found in the GVRD, and since both gases contribute uniformly, the maximum incremental effect of NO_x from BTGP would be about one percent.

Factors complicating any analysis of effects of BTGP emissions on materials are:

- continuity of operation and load on units at the plant;
- wind direction and velocity during operating periods;
- amount and duration of precipitation;
- short-term impingement of pollutants from other sources such as refineries.

In view of the complexity of the interaction of all of these factors, it is not possible to produce any estimate of potential damage more accurate than those given above based on NO_x contributions to the background.

B. Summary of Findings

1. The corrosion rate of bare steel and iron in the GVRD is about 0.25 mpy (0.00025 ipy) as estimated by interpolation of the data in Table 1. The chlorides inherently present in the Vancouver area air will have a minor but significant effect on increasing corrosion. The corrosion of steel and iron is affected by acid gases in the air mass. This value applies to areas where no local polluting emissions can lead to acid gas concentrations significantly above the ambient air levels.

2. Other metals such as zinc and aluminum corrode at somewhat lower rates which are markedly dependent on exposure conditions.

3. Building materials other than metals are not seriously attacked by acid gases in the GVRD. They are attacked by ozone, ultraviolet light, natural rainfall, carbon dioxide, mosses, lichens and the like.

4. The only potentially aggressive pollutant emitted by the BTGP is nitric oxide which is converted ultimately to nitric acid and nitrates. The BTGP at maximum achievable capacity may increase nitrogen oxides in the GVRD by about 5% and nitrogen based acidity by about 3%.

5. The maximum effect of the increase in nitrogen oxides on corrosion of bare steel and iron is about 1%. This is a conservative figure and represents the most severe assumptions of corrosive effects.

6. Airborne chloride particulate may have an additive corrosion effect on the corrosive action of acid gases on construction materials. Such effects probably will outweigh the influence of the incremental nitrogen dioxide due to BTGP.

VI. MONITORING PROGRAM

Corrosion monitoring can be conducted at the existing air quality stations. Because attack on non-metallics is so slow and difficult to quantify, most corrosion (or deterioration) tests are based on metal specimens. For such tests to be meaningful, a long-term program is required (10 years). Typically, the program will involve exposure of a number of metals and will require, in addition to the present pollutant measurements, a continuous measure of time of wetness. Installation of a number of these sites would add to the general background of information on materials performance in the GVRD, and it is possible that new correlations could be developed between corrosion rate and levels of the major pollutants. However, it is doubtful that installation of such a monitoring station to cover BTGP specifically would be justified, and it is also doubtful that meaningful results relating to BTGP would be obtained.

The use of short-term corrosion tests is suspect, and so no consideration should be given to probe-type instruments and the like.

REFERENCES

1. Soderlund, R.
NO_x Pollutants and Ammonia Emissions - A Mass Balance for the Atmosphere over N.W. Europe, Ambio, Vol. VI, No. 2-3, 1977, p.118

2. Abbott, W.H.
Field Versus Laboratory Experience in the Evaluation of Electronic Components and Materials. Paper 234, International Corrosion Forum, NACE, April 1983

3. Gibbons, E.V.
The Corrosion Behaviour of the Major Architectural and Structural Metals in Canadian Atmospheres. Summary of Ten-Year Results of Group I National Research Council of Canada, Division of Building Research. Technical Paper No. 328, 1970.

4. Guttman, H. and Sereda, P.J.
Measurement of Atmospheric Factors Affecting the Corrosion of Metals. Reprint from American Society for Testing and Materials. Special Technical Paper No. 435, 1968.

5. Haynie. F.H., Spence, J.W. and Upham, J.B.
Effects of Air Pollutants on Weathering Steel and Galvanized Steel. A Chamber Study ASTM STP 646, American Society for Testing and Materials, 1978, pp. 30-47.

6. Haynie, F.H. and Upham, J.B.
Correlation Between Corrosion Behavior of Steel and Atmospheric Pollution Data. ASTM STP 558, American Society for Testing and Materials, 1974, pp. 33-43

7. Gibbons, E.V. and Guttman, H.
Corrosion Behaviour of Metal-Coated Panels at Eight Canadian Locations - Summary of a Fourteen Year Program. National Research Council of Canada, Division of Building Research. Technical Paper No. 354, 1970.

8. Guttman, H.
Effects of Atmospheric Factors on the Corrosion of Rolled Zinc. ASTM STP 435, American Society for Testing and Materials, 1968, pp 223-239.

9. Shreir, L.L.
Corrosion, Volume 1 Metal/Environment Reactions. Newnes-Butterworths 1963.

REFERENCES (Continued)

10. Stern, A.C.
Air Pollution, Volume 1. Air Pollution and its Effects. Second Edition, Academic Press 1968.

11. Haynie, F.H.
Effects of Gaseous Pollutants on Materials: A Chamber Study. Environmental Protection Agency, February, 1976.

12. LaQue, F.L. and Copson, H.R.
Corrosion Resistance of Metals and Alloys, Second Addition.

13. Russell, C.A.
Relation of Air-Borne Nitrate to Telephone Equipment Damage, Bel Telephone Laboratories.
Presented before the Division of Water, Air and Waste Chemistry.1 American Chemical Society Chicago, Illinois, 1970.

14. Suzuki, et al.
Studies on Metal Corrosion Caused by Air Pollutants, Part 1. Environmental Science Report, Chiba University, March 1975.

15. Sereda, P.J.
"Weather Factors Affecting the Corrosion of Metals"
Corrosion in Natural Environments, ASTM STP 558, American Societ for Testing and Materials, 1974, pp. 17.

16. Biczok, I.
Concrete Corrosion, Concrete Protection. Eighth Edition, 1972.

17. Air Pollution, 2nd Edition, edited by A.C. Stern, 1968, pp. 636.

18. Emslie, J.H.
Impact Areas of Wet and Dry Deposition, Burrard Thermal Plant, December 8, 1981.

19. Brotherston, A.E. and Emslie, J.H.
Burrard Thermal Generating Plant Air Emissions and Impacts, Report No. ESS-39, April 1982.

20. Vet, R.J., Reid, N.W., Hunt, J.E.
Assessment of the Potential Incremental Acid Deposition in the Greater Vancouver Area from the Burrard Thermal Generating Plant, prepared for B.C. Hydro & Power Authority by Concord Scientific Corp., Oct. 1981.